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**Abstract**:

Zn isotope is a useful tool for tracing biogeochemical processes as zinc plays important role in the biogeochemistry of natural systems. However, Zn isotope composition in the lake ecosystems has not been well characterized. This study aim to investigate the Zn isotope compositions of suspended particulate matter (SPM) and biological samples collected from the Aha Lake and Hongfeng Lake, and their tributaries in summer and winter, in order to explore the potential of this novel isotope system as a proxy for biogeochemical processes in aqueous environments. Concentration of dissolved Zn ranged from 0.65 to 5.06 μg/L and 0.74 to 12.04 μg/L for Aha Lake and Hongfeng Lake respectively, while the SPM-Zn ranged from 0.18 to 0.70 mg/g and 0.24 to 0.75 mg/g for Aha Lake and Hongfeng Lake respectively. The Zn isotope composition in SPM from Aha Lake and its main tributaries ranged from -0.18‰ to 0.27‰ and -0.17‰ to 0.46‰ respectively, and it varied from -0.29‰ to 0.26‰ and -0.04‰ to 0.48‰ respectively in Hongfeng Lakes and its main tributaries, displaying a wider range in tributaries than lakes. From the results and discussion, they implied that Zn isotope composition mainly affected by tributaries inputting in Aha Lake, while adsorption process by algea was major factor for the Zn isotope composition in Hongfeng Lake, and ZnS precipitation leads to the light Zn isotope composition of SPM in summer. These data and results provide the basic information of the Zn isotope for the lake ecosystem, and promote the application of Zn isotope in biogeochemistry.

**Key words**: Zn isotope composition; SPM (Suspended particulate matter); Lake;

Tributary

## 1. Introduction

With the development of MC-ICP-MS, transition metal isotopes have received increasing attention over the last 15 years, and have been successfully applied to trace biogeochemical processes (Luck et al., 1999; Beard et al., 2003; Weiss et al., 2007; Viers et al., 2007; Mattielli et al., 2009; Bigalke et al., 2010; Mathur et al.,2005, 2012; Blätter et al., 2015; Li et a., 2015; Song et al., 2011; Reddy et al., 2015 ). As one of the second most abundant transition metal elements, Zn occurs widely in the atmosphere, soil, rivers, plants and animals (Hutchinson., 1957; Matthys., 1975; Alloway et al., 2004), and is also a critical element for biological functioning (Brand et al., 1983; Olhaberry et al., 1983; Shankar and Prasad, 1998; Hambidge, 2000; Andreini et al., 2006). It has also been demonstrated that Zn participates in multiple biological processes, notably as cofactor in enzymatic photosynthetic reactions (Frausto J J R, 1991). In particular, Zn is a cofactor in the carbonic anhydrase enzyme that catalyzes the conversion between $HCO_3^-$ and $CO_2$ (Brown et al., 1993, Lippard S J, 1994; Nimer N A, 1995). However, it also has detrimental effects on living organisms when present at high concentration (Cloquet et al., 2006).

The fractionation mechanism of Zn isotopes has been studied by many scientists, who have identified three main processes that cause Zn fractionation (Budd et al., 1999; Maréchal et al., 2002a,b; Zhu et al., 2002; Stenberg et al., 2004; Weiss et al., 2005; Pokrovsky et al., 2005; Gélabert et al., 2006; Bryan et al., 2015). Firstly, Zn isotope can be

fractionated during plant uptake (Weiss et al., 2005; Vance et al., 2006) and adsorption processes (Gélabert et al., 2006; Pokrovsky et al., 2005; Kafantaris S C V., 2014). Secondly, zinc adsorption on soil, Mn oxyhydroxide, kaolinite and sediments is an another factor of isotope fractionation (Cacaly et al.,2004; Rousset et al., 2004; Pokrovsky et al.,2005; Bryan et al., 2015; Guinoiseau et al., 2016). Finally, zinc isotope can fractionation during the sphalerite precipitated from the solution or rock material, and also can fractionation during different Zn species, like sulfide, chloride and carbonate (Archer et al., 2004, Wilkinson et al., 2005; John et al., 2008; Jujii., 2011 & 2012). Generally speaking, the range of $\delta^{66}$Zn values in geological materials on Earth is between -0.91‰ to 1.04‰ (Luck et al., 1999; Maréchal et al., 2000; Mattielli et al., 2009; Pichat et al., 2003; Dolgopova et al., 2006; Weiss et al., 2007; John et al.,2007; Mason et al., 2005, little et al., 2016), and it is relatively narrow compare to the lunar samples(-3.83‰ to 6.89‰)(Monyier et al., 2006).

The Zn isotope composition of different materials collected from atmosphere, soil, sediment, ocean, and river, has been analyzed and applied to trace sources of Zn (Maréchal et al., 1999; Maréchal et al., 2000; Dolgopolova et al., 2006; Cloquet et al., 2006; Berimin et al., 2006; Weiss et al., 2007; Sivry et al., 2008; Mattielli et al., 2009; Chen et al., 2009; Thapalia, et al., 2010). It was found that the Zn isotope composition in rainfall is lighter than in carbonatite as early as 1999 (Luck et al., 1999). Zn isotope composition were also combined with lead isotope ratios to trace that the Zn in lichen and birch at Orlovka–Spokoinoe mining district, Eastern Transbaikalia, Russia, mainly comes from the mining area (Dolgopolova et al., 2006). Zn isotopes were investigated in a variety of

stream waters draining mining districts located in the United States and estuary in pairs, and it demonstrated that Zn isotopes maybe used to probe biogeochemical processes (Borrok et al., 2008; Chen et al., 2009). The Zn isotope composition of soils shows that mining areas are a source of heavy metal pollution (Bigalke., et al., 2010). Zn isotope composition of snow, ice and atmosphere indicate that $\delta^{66}$Zn is useful tool in pollution provenance (Mattielli et al., 2009; Voldrichova., et al, 2014). In addition, Zn isotopes composition was also studied in the Ocean to trace the Zn biogeochemical cycle (John et al., 2004; John et al., 2014; Zhao et al., 2014; Little et al., 2016).

However, Zn isotope composition in the lake ecosystem has not been well characterized, besides the research from the eutrophic Lake Greifen, Switzerland (Peel et al., 2009). Accordingly, there is still much work to be done before using Zn isotopes to unravel biogeochemical cycling of Zn in the lake ecosystem successfully. Lakes are easily accessible natural laboratories with well-established biogeochemical processes (Sigg et al., 1985). This work aims to investigate the Zn isotope composition of suspended particle matter (SPM) in Aha Lake and Hongfeng Lake, both are eutrophic and seasonal anoxic lakes, and located at the southwest suburb of Guiyang, Guizhou Province, China. SPM of lakes is a mixture of organic and inorganic detritus, Fe-Mn oxhydroxides, clay minerals, carbonates, phytoplankton, zooplankton, bacteria, and other particles that are retained on 0.45 μm pore size filter. SPM can affect transportation and transformation of trace contaminants among water, sediment and the food chain, hence it is a critical chemical component of the biogeochemical cycling in lakes (Ödman et al., 1999; Turner and Millward, 2002). The Zn isotopic compositions of SPM in Hongfeng and Aha Lakes and

their tributaries were investigated in this research, to assess the behavior of zinc isotopes composition during biogeochemical processes in the aqueous environment.

## 2. Study background and sample collection

### 2.1 study site

Aha and Hongfeng are artificial river interception reservoirs located in southwest of Guiyang city about 8 km and 31.5 km respectively, in a subtropical humid monsoon climate zone. The catchments are characterized by low rainfall and river discharge during winter and spring, whereas high temperatures in summer and autumn bring more rainfall and high river flow (Table1). They are both seasonally anoxic reservoirs. Aha lake covers an area of 4.5 $km^2$ ,with a total water volume of $4.45\times10^7$ $m^3$. The average and maximum depths are 13 m and 24 m, respectively. The residence time of lake water is about 0.44 year. The watershed area is 190 $km^2$ with an average annual precipitation of 1109 mm, and the average annual temperature is 13.8-15.5 °C. Previously, more than 200 coal mines were widely distributed in the watershed, where significant amount of acid mining drainages and dump filtrates were produced. There are six main rivers flowing through the watershed area including five inflowing tributaries, Youyu River (YYR), Caichong River (CCR), Lannigou River (LNR), Baiyan River (BYR) and Sha River (SR), and only one draining river, Xiaoche River (XCR) (Fig1). YYR and BYR are mainly polluted by coal mines, CCR and LNGR are mainly polluted by domestic sewerage, and SR polluted by industrial and domestic sewerage. The surface of lake water is colonized by sparse diatoms and cause eutrophication in summer.

Hongfeng Lake covers an area of 57.2 $km^2$ and much bigger than Aha lake, its

reservoir storage capacity is $6.01\times10^8$ $m^3$, with a drainage area of 1596 $km^2$, the water residence time is about 0.33 year. The average and maximum water depth is 10.52 m and 45 m, respectively. Hongfeng Lake consists mainly of two areas: the North Lake and the South Lake, and there are six main tributaries flowing through the watershed area, including five inflowing tributaries, YCR (Yangchang River), MXR (Maxian River), HLR (Houliu River), MBR (Maibao River), THYR (Taohuayuan River), and one draining river, MTR (Maotiao River) (Fig 1). The discharges of YCR and THYR are larger than others among these tributaries. The industrial wastewater pollution constitutes a more serious impact on the water quality of Hongfeng Lake. In particular, the fertilizer plant of Guizhou is the most serious polluting enterprise, it discharges lots N, P into the lake every year. Accordingly, the lake becomes eutrophic in the spring and summer, as evident from the presence of cyanobacteria and algea.

**2.2 Sampling**

Samples were mainly collected in Aha Lake and Hongfeng Lake and their tributaries (Fig 1). For the Aha Lake, samples were collected at AHLJK (Liang Jiang Kou) as the upstream site and AHDB (Da Ba) as the downstream site. For Hongfeng Lake, samples were collected along the flow direction from south to north, with HFHW (Hou Wu) site of South Lake and HFDB (Da Ba) site of North Lake. The samples were collected with stratified collection at each site; sampling interval with water depth in each site is slightly different, but generally ranged between 3 and 5 meters. Samples of all tributaries were collected at sites near the lake but far away from living areas. All samples were collected in August 2006 (summer) and January 2007 (winter). The algea samples were collected

using nylon net from the surface of the Maxian River (MXR).

All collection wares used in the field were carefully cleaned. Polyethylene bottles, tubes for sample collectors were all soaked in 6 N HCl (GR) for more than three days and then rinsed with 18.2 Ω Milli-Q water. Bottles for sampling were pre-rinsed with the corresponding water samples three times prior to sampling. A multi-parameter sensor was used for determining the pH, water temperature (T), and DO (dissolved oxygen). Water samples for measurement of Zn isotope composition of SPM were collected in 10 liters polyethylene barrels; water samples for determining the concentration of SPM, concentration of Zn and Al in SPM, and speciation of SPM were collected in 1.5 L polyethylene bottles; water samples for analyzing chlorophyll were collected in 50 ml brown glass bottles with two drops of $HgCl_2$ to prevent metabolic activity. Samples for analyzing the dissolved Zn were filtered with 0.45 μm Millipore membrane filter in the field and acidified to pH<2 with ultra-pure $HNO_3$. All samples were transported to laboratory as soon as possible after collection.

## 3. Sample preparation for Zn isotope analysis

The sample preparation work was carried out in a clean room. All the critical work including sample filtration, digestion and purification was completed in class 100 laminar flow hoods. Hydrochloric acid (HCl) was distilled twice in quartz sub-boiling still, Hydrofluoric acid (HF) and Nitric acid ($HNO_3$) were distilled with Teflon two-bottle setup. Milli-Q water (18.2 MΩ) was used throughout the procedures. The filters were treated three times with 1 N HCl (double-distilled), rinsed with Milli-Q water (18.2 MΩ), and then dried at 50°C in an oven and weighted. After those processes, the blank of filters is as low

as 0.001 μg/L and can be negligible.

### 3.1 Sample preparation

The SPM for measurement of Zn isotope composition was isolated by collecting SPM both deposited either on Millipore HA membrane filter (100 mm, 045 μm) or particulate matter that settled at the bottom of the container. The filters with SPM were stored in polyethylene tubes in a fridge. The sample for measuring the concentration of SPM, the speciation of SPM and concentration of Zn and Al in SPM was also filtered through Millipore HA membrane filter (45 mm, 0.45 μm), then dried at 50°C in the oven, and weighed. The volume of water filtered was recorded to calculate the concentration of SPM. Samples for determination of chlorophyll were filtered and chlorophyll quantified following the acetone extraction spectrophotometric method (Barnes et al., 1992). Algea samples were cleaned and dried in a freeze dryer, and then ground to 50 meshes for digestion and $\delta^{66}$Zn analysis.

The speciation of SPM was determined following a sequential extraction procedure (Tessier, et al, 1979). For this, we only extracted three fractions, including adsorption, exchangeable and carbonate bound (AEC) fraction using pH=2 HCl, bound to organic matter fraction using 30% $H_2O_2$ (pH=2), and residual fraction. The extracted solution was evaporated on a hot plate and the solid residue was digested, and then all of them were dissolved in 2% $HNO_3$ for analysis.

### 3.2 Sample digestion

All SPM and algea samples for zinc isotope measurement, concentration of Zn, Al, and the residual fraction of SPM were digested. These samples were soaked with 3 ml aqua

regia and 0.5 ml concentration HF for 48h in acid-cleaned Teflon beakers (7 ml, Savillex). The beakers were placed on a hot plate and dried at 80°C. Another 3 ml aqua regia and 0.5 ml concentration HF were added and the closed beaker was placed on a hot plate for 72h at 140°C for digestion. The procedure was repeated until the particles were thoroughly digested. After samples were digested thoroughly, solutions of sample were left on the hot plate to dry at 80°C. For the zinc isotope measurement samples, the last step was sequentially repeated three times with 0.5 ml concentrated HCl to eliminate $HNO_3$ and HF, and then the residue re-dissolved in 7 N HCl+0.001% $H_2O_2$ for chemical purification. Other samples were just re-dissolved in 2% $HNO_3$ for analysis.

**3.3 Chemical purification**

Chemical purification was carried out using procedures similar to those of Maréchal et al. (1999), Ding et al., (2006) and Tang et al. (2006), with slight modifications. Details are as follow: Anion-exchange chromatography was performed with polypropylene column (Bio-Rad, diameter: 6.8 mm, height 4.3 cm) filled with AG MP-1 resin (Bio-Rad, 100–200 mesh, chloride form). The resin was first cleaned with 2 ml 0.5M $HNO_3$ alternating with 10 ml 18.2 MΩ Milli-Q water three times. Then 5 ml Milli-Q water was used to ensure that the $HNO_3$ was thoroughly removed. The resin was then continuously pre-conditioned with 5 ml 7 N HCl+0.001%$H_2O_2$ and 4 ml 7 N HCl+0.001%$H_2O_2$. Then the prepared samples were loaded on the resin and the matrix were striped with 35 ml 7 N HCl+0.001%$H_2O_2$; Fe was eluted with 20 ml 2 N HCl+0.001%$H_2O_2$, and Zn was eluted with 10 ml 0.5 N $HNO_3$. The Zn eluate was evaporated to dry on a hot plate at 80°C and dissolved in 0.1 N $HNO_3$ to a concentration of 100 to 200 μg/L for isotope analysis. The

recoveries of Zn for all samples were nearly 100%, so the Zn isotope fractionation can be avoid during the purification process (Maréchal et al., 2002b). The procedural blanks including digestion, column purification and evaporation were always less than 0.11% of the total Zn extracted from the samples.

### 3.4 Mass spectrometry

The concentration of dissolved Zn was analyzed on Quadrupole ICP-MS (GV Instruments), and the concentration of Zn and Al in SPM was analyzed on ICP-OES (Varian vista MPX). The Zn isotope composition was analyzed on Nu Plasma instrument HR MC-ICP-MS at Laboratory of isotope Geology, MLR, Institute of Geology, CAGS, Beijing, China. The Zn samples and standard Zn sample, with concentrations ranging from 100 to 200 μg/L in 0.1 N $HNO_3$, were introduced to the argon plasma via a desolvation nebulizer DSN-100 system, with gas flow rates of 50-100 μL/min. The typical ion beams for 200 μg/L Zn solutions of both standards and samples were 4-6 V on $^{64}Zn$ and the blanks were always below 0.005 V. The standard-sample bracketing (SSB) method has been used throughout the study to minimize the instrumental mass bias and the standard-sample concentrations matched within 5%. The performance of the instrument was assessed by repetitive measurements of an internal lab standard (GSB-Zn) relative to the Zn isotope reference material Romil. The average Zn isotope values for GSB Zn is $\delta^{66}Zn$ =6.96±0.11‰, $\delta^{67}Zn$ =10.4±0.23 $\delta^{68}Zn$=13.2‰±0.22 (2SD) in high resolution mode under optimized conditions. The long-term instrumental reproducibility defined from the 7 months' replicate analyses are 0.11‰ for $\delta^{66}Zn$, 0.23‰ for $\delta^{67}Zn$ and 0.22 for $\delta^{68}Zn$. The detailed conditions and the performance of isotope measurements

were described in Li et al. (2008) and Gao et al. (2014).

Zn isotope data was reported in $\delta^{x}Zn$ ($\delta^{66}Zn$, $\delta^{68}Zn$) as parts per thousand deviations relative to JMC 3-0749. All the $\delta^{64}Zn$ and $\delta^{66}Zn$ values obtained in this study followed the theoretical mass-dependent fractionation line, with a formula of $\delta^{68}Zn=1.976\times\delta^{66}Zn+0.0005$ ($R^2=0.9998$).

$$\delta^{66}Zn_{JMC} = \left[ \frac{\left( {}^{66}Zn/{}^{64}Zn \right)_{sample}}{\left( {}^{66}Zn/{}^{64}Zn \right)_{JMC}} - 1 \right] \times 1000$$

## 4. Results

### 4.1 Temperature, DO (Dissolved Oxygen), pH and chlorophyll in Aha Lake and Hongfeng lakes, and their tributaries.

Environment parameters are summarized in Table 1, and plotted in Figs. 2 and 3. In summer thermal stratification was observed in August with a temperature gradient of ca. 10°C in Aha Lake. The thermoclines were located at a water depth ca. 10m for AHDB and ca. 6m at for AHLJK station. Dissolved oxygen declined sharply below the thermoclines, with average concentration ca.1.2 mg/L in Aha Lake, and there was also a marked decrease in pH of ca. 0.5 units below the thermocline for AHDB profile. However, there were no clear depth-dependent variations in temperature, DO and pH in the winter both for AHDB and AHLJK profiles (Fig 2). Moreover the temperature gradient was ca. 6°C from surface water to thermocline for Hongfeng Lake, and the thermocline was located at a water depth ca. 12m for HFHW station in summer. DO was also almost depleted under the thermocline, with average concentration of 2.0 mg/L, and hypoxic conditions prevailed

in summer. There was also marked decrease of ca. 2 units in the deep layers at Hongfeng. However, there were also no clear depth-dependent variations in temperature, dissolved oxygen and pH in the winter for Hongfeng Lake in winter (Fig 3).

The concentration of chlorophyll was measured for both Aha Lake and Hongfeng Lake. In summer, the concentration of chlorophyll was very high, reaching 42.1 μg/L at surface water, with marked decreasing to 5.2 μg/L at the bottom for HFHW station, while the concentration of chlorophyll varied from 11.1 to 2.1 μg/L for AHDB station. It is apparent that eutrophication occurred at the surface of Hongfeng Lake in summer (Figs 2 and 3).

Temperature, DO and pH were also measured for all tributaries. The temperatures of most tributaries were similar to that of the thermocline of the lake, and concentrations of DO for most rivers in summer were lower than in winter.

**4.2 SPM concentration, Zn in dissolved and SPM, and speciation Zn in SPM for Aha Lake and Hongfeng Lake.**

The average concentration of SPM was 1.88 and 2.73 mg/L in summer for AHDB and AHLJK profiles respectively, it was higher than in winter(average is 1.02 and 0.98 mg/L for AHDB and AJLJK respectively), and it decreased with increasing water depth in summer. Similarly, the average concentration of SPM was 2.79 mg/L in summer for HFHW, it was also higher than in winter (average is 1.96 mg/L), and the concentration was higher at the surface than bottom in summer (Tables 1 and 2, Figs 2 and 3.).

Dissolved Zn ranged from 0.65 to 5.06 μg/L and 0.74 to 12.04 μg/L for Aha Lake and Hongfeng Lake respectively, the SPM-Zn ranged from 0.18 to 0.70 mg/g and 0.24 to 0.75

mg/g (Figs 2 and 3). Generally speaking, the concentration of Zn in Hongfeng Lake was higher than in Aha Lake, but dissolved Zn concentration did not exceed regulatory limits in both lakes, in contrast to Yellow River and Greece Kalloni bay (Hong et al, 2006; Gaverill et al., 2005). Dissolved Zn was slightly higher in winter than in summer, but there was no significant variation with water depth for Aha Lake. Meanwhile, average of SPM-Zn in summer was very similar to that in winter. Dissolved Zn in winter was higher than in summer for Hong Lake, which was similar to Aha Lake; while average of SPM Zn in summer was slightly higher than in winter for Hongfeng Lake (Fig 2 and 3).

The speciation of Zn in SPM also was determined. It was found that AEC-bound Zn ranged from 57.4 to 94.7% and 29.1 to 90.1% for Aha and Hongfeng Lake respectively (table2 and Fig4). The percentage of organic bound Zn averaged 17.1% in summer, higher than average 7.4% in winter for AHDB station. In addition, the percentage of organic bound Zn reached 53.1% at subsurface water and averaged 14% in summer for HWFW station, higher than the average 7.4% in winter at Hongfeng Lake, which is analogous to HFHW station.

Concentration of SPM, dissolved Zn and SPM-Zn varied significantly in time and space (Table 3). For Aha Lake, SR and YYR had the higher SPM (78.03 mg/L and 65.93 mg/L) and YYR (18.07 μg/L) had the highest dissolved Zn content than other rivers. The concentrations of SPM and dissolved Zn in summer were higher than in winter for most rivers, and concentration of SPM-Zn varies between summer and winter. In addition, average dissolved Zn (5.3 μg/L) and SPM-Zn (0.51 mg/g) of Aha tributaries were higher than Aha Lake (2.03 μg/L and 0.36 mg/g, respectively). For Hongfeng Lake, THYR had

highest SPM (9.4 mg/L) and dissolved Zn content (14.78 μg/L) concentration than other rivers. The concentration of dissolved Zn in winter was higher than in summer for most of rivers, and THYR also had the highest SPM-Zn content (2.9 mg/g). Moreover, average dissolved Zn (4.63 μg/L) in Aha lake was similar to that in Hongfeng Lake (5.73 μg/L), but average SPM-Zn (0.70 mg/g) was higher than in the Hongfeng lake (0.40 mg/g).

**4.3 Zn isotope composition in Hongfeng, Aha lakes and their tributaries**

The Zn isotope composition of SPM varied significantly in time and space. Generally speaking, $\delta^{66}$Zn of SPM ranged from -0.29‰ to 0.55‰ for these samples which collected from Aha Lake and Hongfeng Lake and their tributaries, the variation is about 9-10 times compared to precision of determination. This falls largely within the previously determined isotope range of particle Zn from Greifen Lake (-0.66‰ to 0.21‰) and Seine river (-0.08‰ to 0.30‰), but slightly lighter than terrestrial geological material (0.4‰ to 1.4‰)(Peel et al., 2009; Chen et al., 2009; Cloquet et al., 2006; litter et al., 2016). All the $\delta^{66}$Zn data for SPM from Aha Lake and Hongfeng Lake are given in Table 1 and $\delta^{66}$Zn data for SPM from tributaries are given in Table 3.

The Zn isotope composition of SPM for Aha Lake ranged from -0.18‰ to 0.27‰, slightly lighter than Aha tributaries. The Zn isotope composition in the summer (-0.18‰ to 0.19‰) was lighter than in winter (0.03‰ to 0.27‰) for Aha Lake. The Zn isotope composition of SPM for Hongfeng Lake ranged from -0.29‰ to 0.26‰, and it was also slightly lighter than the Zn isotope composition of SPM in Hongfeng tributaries (-0.04‰ to 0.48‰). Similarly, the $\delta^{66}$Zn varied from -0.29‰ to 0.20‰ for Hongfeng Lake in summer, also slightly lighter than the $\delta^{66}$Zn in winter (Figs 2, 3, Table 1).

For Aha Lake, there were no discernible trends with increasing water depth both in AHDB and HALJK stations in winter, but it was apparent that the heavier $\delta^{66}Zn$ appeared at the surface for AHDB, which was similar to the HFHW in summer. Whereas, there was also a clear increase of $\delta^{66}Zn$ with water depth for AHLJK station in summer. For the Hongfeng Lake, there were no clear trends with depth in winter for both sites HFHW and HFDB. However, a pronounced decrease of $\delta^{66}Zn$ was observed with increasing water depth to -0.29‰ at a depth of 12 m in summer at HFHW station. Lower $\delta^{66}Zn$ appeared at the thermocline while the higher $\delta^{66}Zn$ appeared at the surface. This trend was similar to that of particles collected from Atlantic and Pacific Oceans (Maréchal et al., 2000).

The Zn isotope of SPM in tributaries also varied significantly in time and space. For Aha Lake, the $\delta^{66}Zn$ of YYR and BYR were -0.09‰ and -0.17‰ in summer respectively, which were isotopically light relative to sphalerite (0.02‰ to 0.44‰), but same as the pyrite (-0.19‰ to -0.19‰) (Maréchal et al., 1999). In addition, YYR and BYR have lighter $\delta^{66}Zn$ in summer than in winter. However, the $\delta^{66}Zn$ of CCR was 0.34‰ in summer, which was isotopically heavier than in winter (0.10‰). For the only draining river of the Aha Lake, XCR had similar $\delta^{66}Zn$ value in summer and winter.

For Hongfeng Lake, THYR and YCR had slightly heavier Zn isotope of 0.40‰ in summer than in winter (0.25‰ and 0.04‰), and the $\delta^{66}Zn$ of MXR in summer (0.30‰) was slight lighter than in winter (0.48‰) in contrast. Moreover the MTR and HLR had similar $\delta^{66}Zn$ value in summer and winter. Two algea samples had similar Zn isotope composition of 0.41‰ and 0.40‰ respectively, and the $\delta^{66}Zn$ of algea collected from MXR was 0.21‰.

## 5. Discussion

SPM in lake water is mainly supplied by fluvial input, plankton and inorganic materials produced within the lake (autochthonous material), and sediment resuspension (Hakanson and peters, 1995, Sigg et al., 1995; Riemann et al., 2005). Aha Lake and Hongfeng Lake have surface area of 4.5 $km^2$ and 57.2 $km^2$, water depth of 14 to 24 m and 10 to 45 m respectively, as well as temperature gradients of >10 °C (Fig 2 and 3), which implied that wind induced resuspension of sediment will have limited contributions. Furthermore, Aha and Hongfeng both are seasonal anoxic lakes, therefore our discussion will focus on fluvial, plankton and seasonal anoxic controls.

**5.1 Effect of Zn fluvial input from Tributaries on $\delta^{66}$Zn of SPM**

The Zn contents were normalized to Al to determine Zn enrichment due to non-detrital inputs since Al concentration is a good indicator of detrital input (Chen et al., 2009). Here we investigated the relation between $\delta^{66}$Zn and Zn/Al (Fig 5). The Zn/Al ratio of Aha Lake ranged from 0.007 to 0.153 and average was 0.045, it was much higher than Zn/Al in Hongfeng Lake (average was 0.0145), and indicating SPM Zn was more enriched in Aha Lake than in Hongfeng Lake.

For the Aha Lake, including AHDB and AHLJK Profile in summer, a clear negative relationship between $\delta^{66}$Zn and Zn/Al can be observed (Fig 5). Samples in summer showed higher Zn/Al ratio and lighter Zn isotope composition, whereas samples in winter showed lower Zn/Al ratio and heavier Zn isotope composition. As the discharge of YYR, BYR and SR are relatively bigger than other rivers, the $\delta^{66}$Zn of SPM for Aha Lake maybe controlled by these rivers. The discharge (1.18 $m^3$/s) of YYR is largest of any other rivers, and it mainly contaminated by coal mine and with bigger discharge and high SPM

concentration, displays a higher Zn/Al and lighter Zn isotope in summer, and represents the detrital input from the coal mine, thus the $\delta^{66}$Zn of SPM maybe effected by inputting of the YYR with the coal mine. By contrast, SR displayed lower Zn/Al ratio and heavier Zn isotope, and represents input from domestic and industrial activities, Its $\delta^{66}$Zn (0.05‰ and 0.29‰) were close to anthropogenic samples, ranging from 0.08‰ to 0.31‰ (Chen et al., 2009). Comparing the discharge and concentration of SPM of SR (0.83 $m^3$/s and 78.03 mg/L respectively) river with BYR (0.90 $m^3$/s and 4.53 mg/L) (Table 2), shows that the discharge of them were similar, but the concentration of SPM of SR was almost 18 times higher than BYR. Therefore the main SPM source was likely to be SR, and $\delta^{66}$Zn of SPM likely to be affected by the inputting of SR with domestic and industrial waste water. Consequently, $\delta^{66}$Zn of SPM for Aha Lake mainly be affected by mixing of YYR and SR process (Fig 5).

We further investigated the relationship between $\delta^{66}$Zn of SPM and the Residual Zn of SPM (Fig 6), since the residual fraction of metals comes mainly from primary and secondary minerals in which trace metals are not expected to be released in solution over a reasonable time under natural conditions (Tessier et al., 1979). Thus, the residual form of SPM may represent the material from background or terrigenous sediment (Ödman et al, 1999; Turner and Millward, 2002; Tessier, 1979).

We can see clearly that there was linear relationship between Zn isotope composition and residual fraction of Zn in Aha Lake (Fig 6). There were a positive relationship between Zn isotope composition and residual fraction of Zn in summer for AHDB, and a negative relationship in summer and positive relationship in winter for AHLJK. Although there were

little data, and they are not significantly correlated with each other, we still can obtain some information from these data. As mentioned above, the main input tributarie was SR for AHDB profile, therefore the main SPM source of AHDB is likely to be SR. According to the Zn isotope composition of SR (0.29‰) and AHDB profile (-0.05‰ to 0.19‰), the Zn isotopic composition of SR are heavier than AHDB profile in summer, thus it lead to positive relationship between Zn isotope composition and residual Zn at AHDB. Consequently, we can draw the Zn isotope composition of SPM for AHDB was mainly affected by input of SR. Similarly, YYR was the main source of AHLK profile according the table 3. Comparing the Zn isotope composition of YYR in summer (-0.09‰) to that in winter (0.46‰), we can obtain that YYR had light Zn isotopes in summer and acts as a heavy Zn isotope source in winter, consistent with a negative correlation in summer and positive correlation between $\delta^{66}$Zn and Zn/Al in winter for AHLJK profile(Fig 6). Accordingly we can draw the Zn isotope composition of SPM for AHLJK was mainly affected by inputting of YYR. These conclusions were agree with these from the relation between $\delta^{66}$Zn and Zn/Al of SPM, and further approved that Zn isotope composition of Aha Lake was mainly affected by SR and YYR, and it is a mixing of endmember process.

By contrast, there was no correlation between Zn/Al and Zn isotope composition of SPM in HFHW and HFDB both in summer and winter and there were no significant variations of Zn/Al ratio for all samples in Hongfeng Lake. Furthermore, there still was no clear correlation between $\delta^{66}$Zn and residual Zn of SPM in Hongfeng Lake

The $\delta^{66}$Zn of MXR, THYR and YCR in summer were isotopically heavier than $\delta^{66}$Zn in Hongfeng lake, however there was no clear relationship between tributaries and the

Hongfeng Lake (Fig5 and Fig6). Therefore there was no significant effect on Zn isotope composition come from fluvial input in Hongfeng Lake.

From above discussion, we accordingly draw the conclusion that Zn isotope composition at Aha Lake was mainly controlled by inputting of YYR with coal mine input and SR with the domestic and industrial particulate input, whereas the Zn isotope composition was not necessarily affect by fluvial inputting for Hongfeng Lake.

**5.2 Effect of algal activities on Zn $\delta^{66}$Zn of SPM**

The $\delta^{66}$Zn of SPM depth profile above the thermocline at HFHW profile in summer showed surface SPM had the heaviest Zn isotope composition, and $\delta^{66}$Zn gradually decreasing with depth. Similarly for AHDB profile, the heaviest $\delta^{66}$Zn of SPM appeared at the surface in summer, and then there was a drop at the sub-surface. These similar phenomena that $\delta^{66}$Zn decreased with depth were found for particle samples in Central Atlantic Ocean (Maréchal et al., 2000), and that $\delta^{66}$Zn of seawater decreased with water depth above 100 m in the North east Pacific Ocean (Bermin et al., 2006), were thought to be mainly related to the activity of phytoplankton. In addition, the $\delta^{66}$Zn of seawater increased with water depth in North Atlantic Ocean, it was also related to phytoplankton and organic matter (John et al., 2014).

In summer, the lake water was stratified; the temperature, pH and dissolved oxygen decrease with depth, and the algal proliferate in the surface water of Hongfeng Lake (Fig 3). Therefore, the variation in $\delta^{66}$Zn in Hongfeng Lake may be related to the algal activities.

Zn isotope fractionation by biological processes occurs by preferential adsorption of

the heavy Zn isotope onto the surface of diatoms, and by the preferential incorporation of the light isotope into biological material (Gélabert et al., 2006; Weiss et al., 2005). Hence, we examined whether there was a correlation between Zn isotope composition and chlorophyll, as chlorophyll is an important indicator of primary producers of phytoplankton biomass, and is the main pigment of photosynthetic phytoplankton (Reynold, 1984; Kasprzak et al., 2008) .

Figure 7 showed that that when the concentration of chlorophyll was low in winter, the Zn isotope composition of SPM was heavy, when concentration of chlorophyll was high in summer, the Zn isotope composition of SPM was light($\Delta\delta^{66}Zn_{winter\text{-}summer}$=0.17‰ for Aha Lake, $\Delta\delta^{66}Zn_{winter\text{-}summer}$=0.07‰ for Hongfeng Lake). Moreover, a significant positive relationship was evident between $\delta^{66}Zn$ and chlorophyll at HFHW profile in summer, and there was no relationship between $\delta^{66}Zn$ and chlorophyll in AHDB and AHLJK profiles in summer. It was notable that the biomass of phytoplankton in Hongfeng Lake was much higher than in Aha Lake in summer (Fig. 7), suggesting that phytoplankton play a major role in controlling Zn isotope variability for Hongfeng Lake in summer.

How the algea affect the Zn isotope composition during the biogeochemical process remains unclear？ Maréchal et al (2000) thought $\delta^{66}Zn$ of particle decreasing from surface to bottom may be caused by activity of phytoplankton and remineralization, and John was aware that the incorporation by phytoplankton mainly accounts for the $\delta^{66}Zn$ of seawater increasing with the depth of water(John et al., 2014). At here, we can discuss from absorption and adsorption processes to explain the Zn isotope variation of SPM for Hongfeng Lake in summer, and to compare which one is the major control factor.

Firstly, the Zn isotope composition of SPM in Hongfeng Lake in summer whether affected by incorporation into algal process? On one hand, as algal incorporation is expected to produce lighter Zn isotope composition of SPM in surface water relative to bottom water according to other research (Gélabert et al., 2006; Weiss et al., 2005). However, our data showed that the Zn isotope of SPM at surface water was heavier than bottom water at HFHW and AHDB in summer (Figs 2 and 3). Hence it was contradictory that absorption was major control factor on the Zn isotope composition. On the other hand, Organic-bound Zn was 12.53% on average, which is much lower than AEC-bound Zn (69.87% on average) (Fig 4), and this further illustrates that effect of algal absorption process on the Zn isotope is minor than adsorption process.

Secondly, the Zn isotope composition was possible affected by the adsorption onto the surface of algea. AEC-bound Zn accounts for 69.87% of the total SPM Zn (Table 2) for HFHW profile, which indicated the Zn isotope composition of SPM being controlled by adsorption process. Generally speaking, the adsorption processes contain abiotic adsorption onto the mineral particle (goethite, hematite and birnessite) and biotic adsorption onto the surface of phytoplankton (Pokrovsky et al., 2005a, b; Gélabert et al., 2006; Weiss et al., 2005). The Zn isotope fractionation exceeds 0.5‰ from surface water to deeper water at HFHW profile, as Zn isotope fractionation does not exceed 0.5‰ during adsorption onto most mineral particles (Pokrovsky et al., 2005; Guinoiseau et al., 2016), thus adsorption onto abiotic surfaces was not the main cause for the variation in Zn isotope composition, whereas adsorption onto algea can be the major factor. Zn isotope can be fractionated during preferential adsorption heavy Zn onto diatoms and plankton

(Maréchal et al., 2000; Pokrovsky et al., 2005; Gélabert et al., 2006; Balistrieri et al., 2008; Juillot et al., 2008). This occurs because during adsorption onto diatoms surfaces, Zn reduces its coordination number from six (octahedrally coordinated to $H_2O$ in bulk solution) to four (oxygen and nitrogen tetracoordinated complexes), so the bond distance becomes shorter while bond strength increases, hence the heavy isotope preference join with stronger metal binding species (Criss, et al., 1999; Young and Ruiz et a., 2003). Therefore, an increase of algea leaded to heavier Zn isotope composition at surface of HFHW in summer (Fig.3). In addition, the $\delta^{66}$Zn of algea in MXR ranged from 0.21 to 0.41‰ (table2), and it was isotope heavier than in Hongfeng Lake, also can explained by adsorption process. Consequently，adsorption onto algea is the major effect factor for the Zn isotope composition in Hongfeng Lake in summer.

For Aha Lake, algal biomass was relatively small in summer, so there was no relationship between Zn isotope composition and chlorophyll. However, this interpretation remains to be confirmed given that our data were reported firstly for lake water column. In the absence of isotope data on dissolved Zn due to the low concentration, it is premature to argue about whether isotope fractionation between biologic particles and lake water takes place at equilibrium or by purely kinetic control. Therefore, much work is still required to develop a full understanding of the use of Zn isotope in lake biogeochemistry and material recycling processes.

**5.3 The effect of seasonal anoxia and ZnS predicated on Zn isotope composition.**

So far, we can conclude from sections 5.1 and 5.2 that Zn isotope composition was mainly affected by the tributary input for Aha Lake, whereas the Zn isotope composition

for Hongfeng Lake was mainly affected by algal adsorption. However, we saw in Fig 3 that the Zn isotope composition of SPM in summer was lighter than in winter for both Hongfeng and Aha Lakes. This result was very similar to $\delta^{66}Zn$ seasonal variation in SPM from Lake Greifen, Switzerland (Peel et al., 2009), and $\delta^{56}Fe$ value of SPM were also lower in summer than in winter in Aha Lake(Song et al., 2011). Nevertheless, both of the tributary input and algal adsorption can't account for this phenomenon. Instead, it implied that the Zn isotope composition of Hongfeng and Aha Lake in summer may be affected by another factor.

As previous studies that Zn isotope can fractionation during process of sphalerite precipitation, and sphalerite preferential incorporation of light Zn isotope(Archer et al,2004; Wilkinson et al., 2005; Kelley et al.,2004; John et al., 2008; Jujii et al., 2011 & 2012). Archer investigated that ZnS precipitated in an anoxic environment at room temperature can fractionated the Zn isotope, and the $\Delta\delta^{66}Zn_{ZnS\text{-}dissolved}$= 0.36‰. (Archer et al.,2004); Wilkinson and Gagnevin also found the rapid sphalerite precipitation from the fluid or ore system result in light Zn isotope (Wilkson et al., 2005; Gagnevin et al., 2012; Kelley et al., 2009); John studied that subsurface cooling of hydrothermal fluids leads to precipitation of isotopically light sphalerite (Zn sulfide), and this process is a primary cause of Zn isotope variation in hydrothermal fluids(John et al., 2008); Fujii investigated the $\delta^{66}Zn$ in different species, like aqueous sulfide, chloride, and carbonated species using ab initio methods, and negative $\delta^{66}Zn$ down to at least -0.6‰ can be expected in sulfides precipitated from solution with pH>9(Fujii et al., 2011 & 2012).

Aha Lake and Hongfeng Lake both are seasonal anoxic lakes. The concentration of

DO (dissolved oxygen) were range from 1.60 to 7.80 mg/L, and average was 4.2 mg/L for Aha Lake in summer, which was much lower than in winter(the concentration of DO were range from 7.7 to 9.0 mg/L and average is 8.6 mg/L). For Hongfeng Lake, The concentration of DO were range from 1.0 to 8.1 mg/L and average was 3.6 mg/L in summer, which was also much lower than in winter( average was 12.7 mg/L). In addition, the concentration of DO deceased from surface to bottom rapidly for all profiles(AHDB, AHLJK, HFHW and HFDB), and the DO only 1.0 mg/L and depth of 15 m in HFHW in summer, the bottom of Lakes were depleted oxygen in summer. This seasonal anoxic characteristic was also appeared in Baihua Lake and Black Sea (Bai et al., 1996; Sun and Wakeham, 1994). At this anoxic condition in summer, SRB (sulfate reducing bacterial) can reduce the $SO_4^{2-}$ to $S^{2-}$(Sass et al., 1997; Bailey et a., 2017), thus Zn can be precipitated from the water, and exist as the species of the sphalerite (ZnS) in the SPM, and this can be approved by the concentration of dissolved Zn was lower in summer than in winter (Fig2 and Fig3). As discussed above, The sphalerite (ZnS) preferential incorporated the light Zn isotope during the precipitation process, therefore the Zn isotope composition of SPM should be light in summer than in winter, and this conclusion coupled with our $\delta^{66}$Zn data for both Aha Lake and Hongfeng Lake. This maybe account for why the $\delta^{66}$Zn in summer was lower than in winter.

## 6. Conclusion

This study described seasonal variation of $\delta^{66}$Zn values for Hongfeng and Aha Lakes, as well as data for tributaries and biological samples, and arrived following conclusions.

Concentration of dissolved Zn ranged from 0.65 to 5.06 μg/L and 0.74 to 12.04 μg/L for Aha and Hongfeng Lake respectively, while the SPM-Zn ranged from 0.18 to 0.70 mg/g and 0.24 to 0.75 mg/g for Aha and Hongfeng Lake respectively. The $\delta^{66}$Zn of SPM ranged from -0.29‰ to 0.26‰ for the Hongfeng Lake and its tributaries respectively, the $\delta^{66}$Zn of SPM ranged from -0.18‰ to 0.27‰ and -0.17‰ to 0.46‰ for the Aha Lake and its tributaries, displaying a wider range in tributaries than lakes.

From the relation of $\delta^{66}$Zn versus Zn/Al and $\delta^{66}$Zn versus residual-bond Zn, we conclude that Zn isotope composition of Aha Lake is mainly affected by SR and YYR, and it is a mixing of endmember process. Discussion the relation of $\delta^{66}$Zn versus chlorophyll and proportion of AEC-bond Zn, it suggests that Zn isotope composition of Hongfeng Lake mainly controlled by the adsorption process of algea. As sphalerite (ZnS) preferential incorporated the light Zn isotope during the precipitation process, this can account for why the $\delta^{66}$Zn in summer is lower than in winter.

In summary, Zn isotopes composition in Aha Lake and Hongfeng Lake are reported firstly, and the major affect factors are discussed, this providing the basic information of Zn isotope in lake system, and promoting the application of Zn isotope in biogeochemistry.

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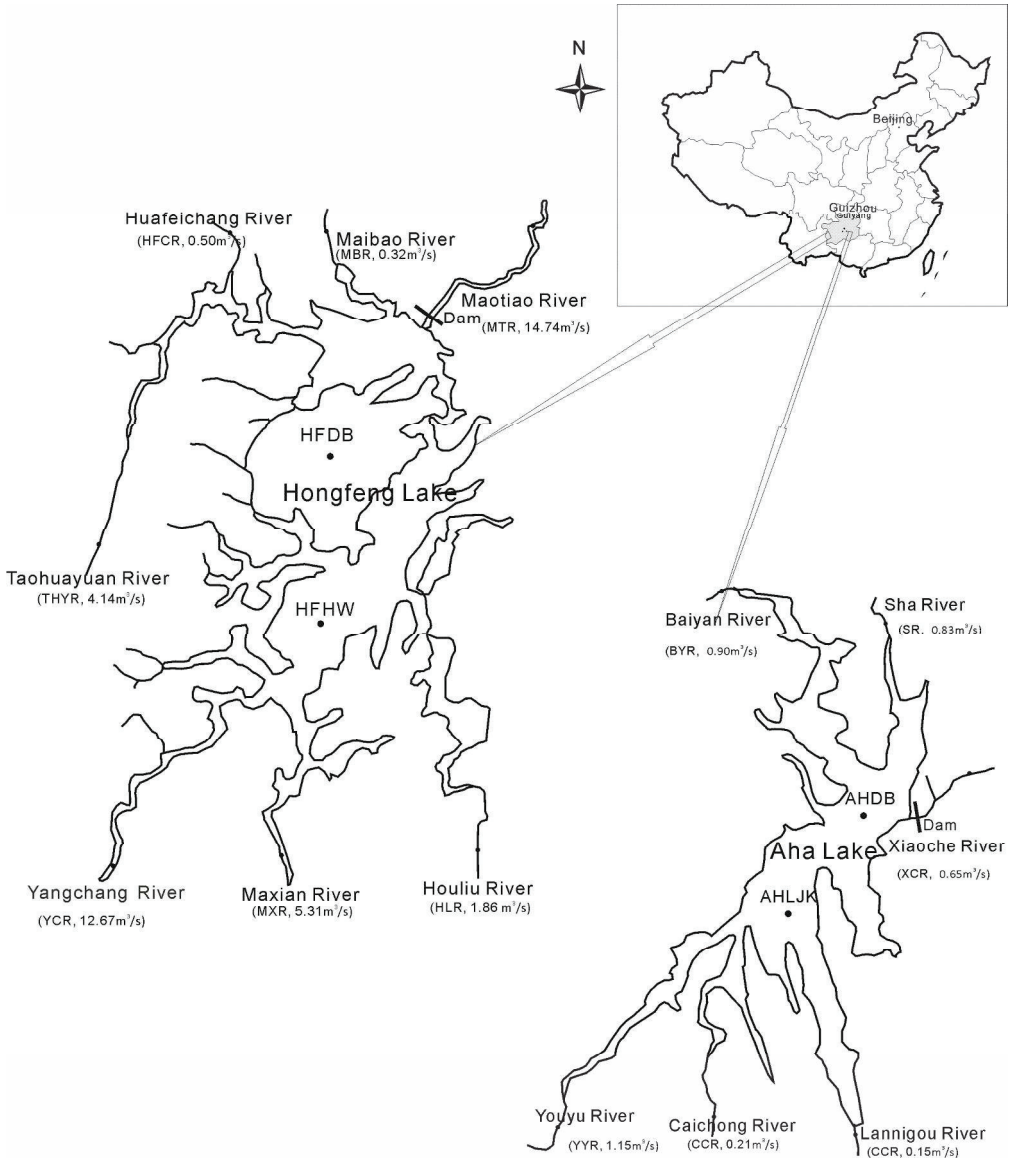


Fig. 1. Location map of Aha Lake and Hongfeng Lake, southwest of China. Shown together in the map are their main, discharges of tributaries and the sampling sites. The sampling locations were AHDB (Da Ba) and AHLJK (Liang jiang kou) profiles in Aha Lake; HFDB (Da Ba) and HFHW (How Wu) profiles in Hongfeng Lake.

207x239mm (300 x 300 DPI)

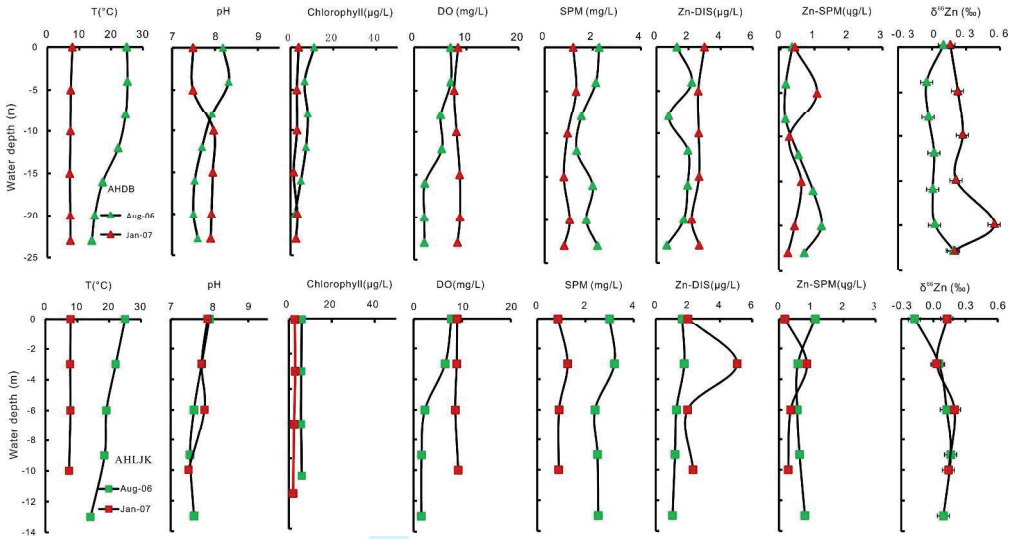


Fig. 2. Plots of Temperature, pH, Chlorophyll, DO (Dissolved Oxygen), Concentration of SPM, concentration of dissolved Zn, concentration of SPM Zn and $\delta^{66}$Zn of SPM (suspended particulate matter) for AHDB and AHLJK profile of Aha Lakes. For both profiles, green triangle and red triangle refer to date of August 2006 and January 2007 for AHDB, respectively; while green square and red square refer to date of August 2006 and January 2007 for AHLJK, respectively.

351x185mm (300 x 300 DPI)

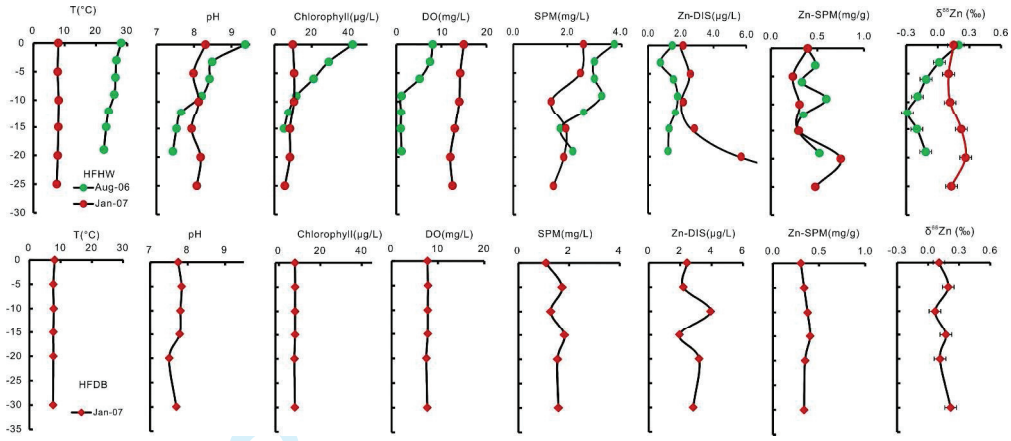


Fig. 3. Plots of Temperature, pH, Chlorophyll, DO(Dissolved Oxygen), concentration of SPM, concentration of dissolved Zn, concentration of SPM Zn and $\delta^{66}$Zn of SPM(suspended particulate matter) for HFHW and HFDB of Hongfeng lake. For both profiles, green circles and red circle refer date of August 2006 and January 2007 for HFHW, respectively, while red diamond refer to date of o January 2007 for HFDB.

356x152mm (300 x 300 DPI)

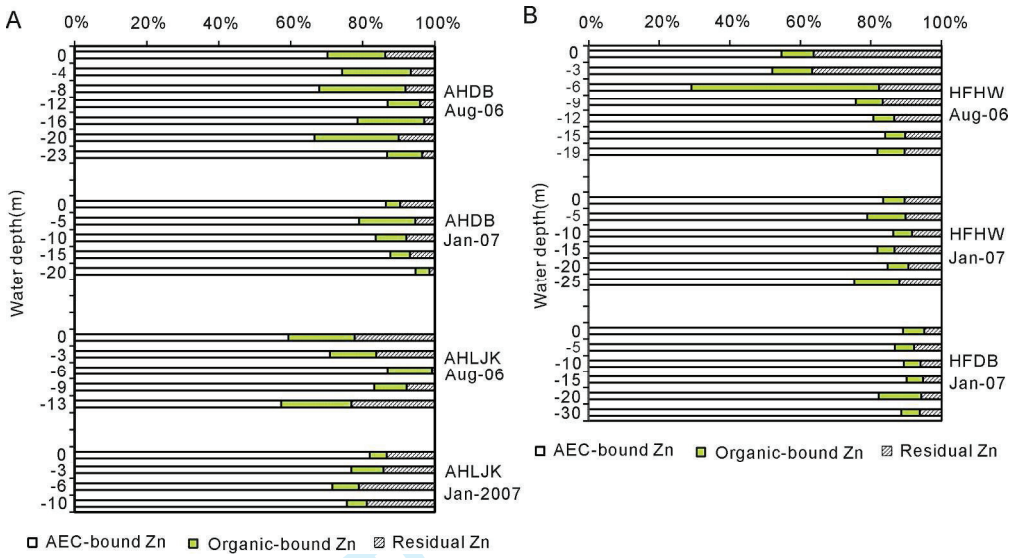


Fig. 4. The proportion of Zn different speciation of SPM. Plot A is the proportion of Zn different speciation of SPM for Aha Lake, while plot B is for Hongfeng lake. For both of two lakes, the open columns refer to AEC-bound Zn, green columns refer to organic-bound Zn, and slash column refer to the residual-bound Zn.

208x114mm (300 x 300 DPI)

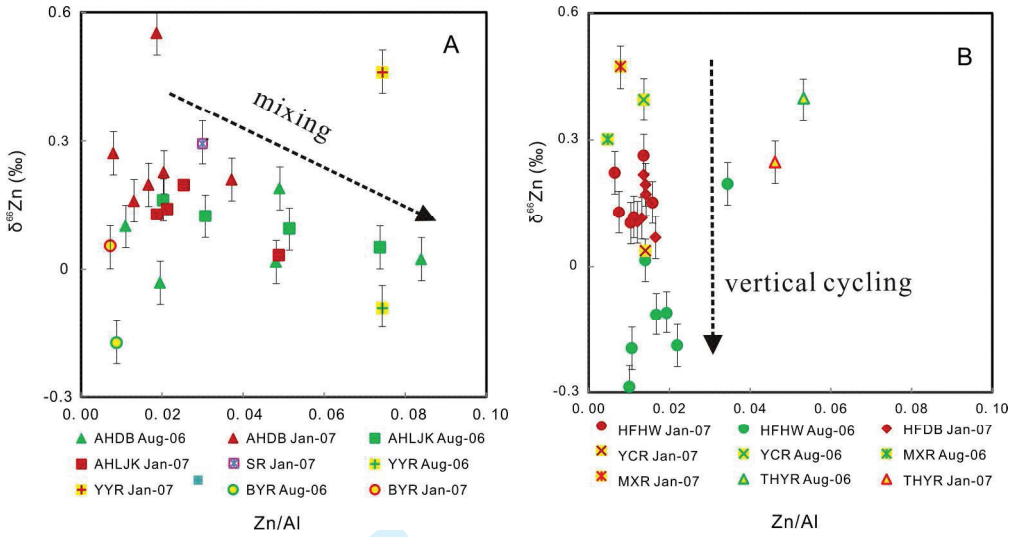


Fig. 5. Relation between Zn isotope composition of SPM and Zn/Al ratio. Plot A is for Aha Lake and plot B is for Hongfeng Lake. For plot A, data points for SPM of AHDB in summer is green triangle, AHDB in winter is red triangle, AHLJK in summer is green square, AHLJK in winter is red square. In addition, the date of YYR, SR and BYR were plotted, as their discharges are bigger than other rivers. For plot B, data points for SPM of HFHW in summer is green circle, HFHW in winter is red circle, HFDB in winter is red diamond, and date of YCR, THYR and MXR are plotted as they are the main tributaries of Hongfeng Lake.

232x121mm (300 x 300 DPI)

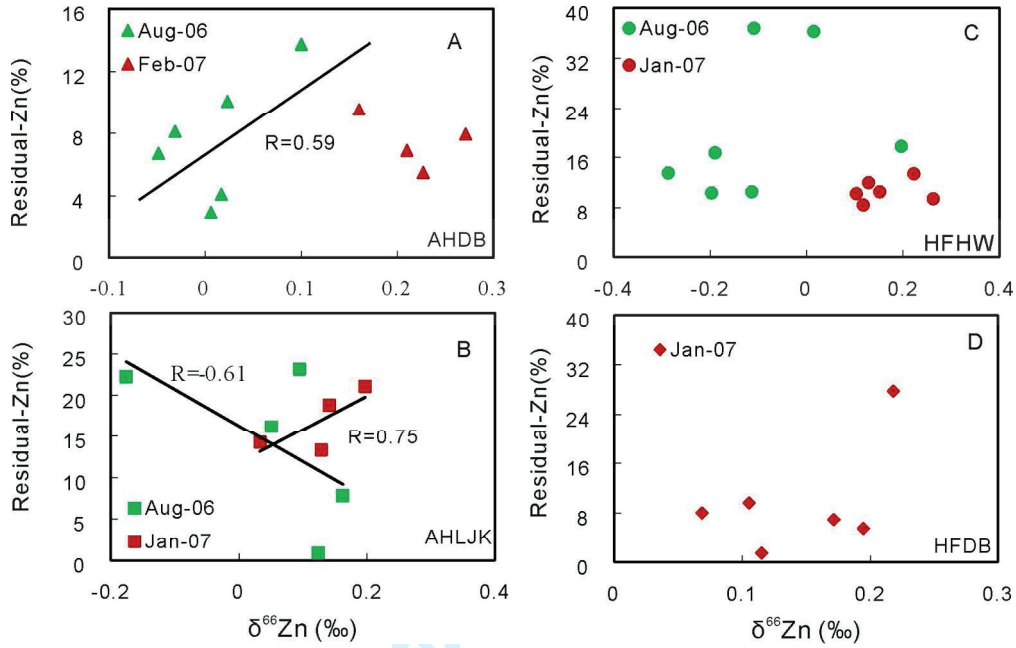


Fig .6. The $\delta^{66}Zn$ versus to residual bound Zn of SPM. The A and B refer to for AHDB and AHLJK profiles respectively, and the C and D refer to HFHW and HFDB profiles. The green triangle and red triangle refer to the data in summer and winter respectively for AHDB respectively, and the green square and red square refer to the data in summer and winter for AHLJK respectively. The green circle and red circle refer to the date in summer and winter for HFHW respectively and red diamond refer to the date in winter for HFDB.

159x101mm (300 x 300 DPI)

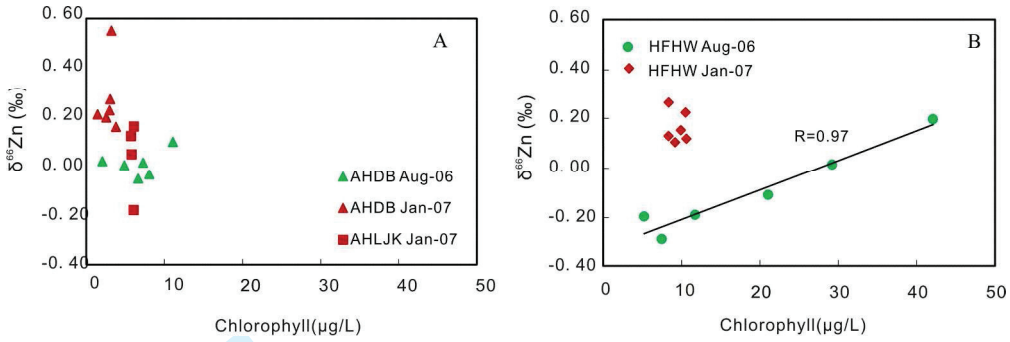


Fig. 7. The $\delta^{66}Zn$ of SPM versus to chlorophyll in Aha and Hongfeng Lakes. Plot A is for Aha and Plot B is for Hongfeng Lake. The green triangle and red triangle refers to the data in summer and winter for AHDB respectively, the green square and red square refer to the data in summer and winter for AHLJK respectively, the green circle and red circle refer to the date in summer and winter for HFHW respectively, and red diamond refer to the date in winter for HFDB.

205x67mm (300 x 300 DPI)

Table1. pH, temperature, DO(dissolved oxygen), concentration chlorophyll, SPM and dissolved Zn in summer and winter for Aha Lake and Hongfeng Lake, southwest of China.

| Sample site | Sampling date | Depth | pH | T(℃) | DO | Chlorophyll | SPM | Zn(DIS) |
|---|---|---|---|---|---|---|---|---|
| SPM | | m | | (℃) | mg/L | mg/L | mg/L | μg/L |
| AHDB | Aug | 0 | 8.19 | 25 | 7.00 | 11.08 | 2.27 | 1.28 |
| AHDB | Aug | -4 | 8.32 | 25.2 | 7.04 | 6.64 | 2.13 | 2.21 |
| AHDB | Aug | -8 | 7.93 | 24.6 | 5.11 | 8.06 | 1.53 | 0.77 |
| AHDB | Aug | -12 | 7.7 | 22.3 | 5.32 | 7.26 | 1.33 | 1.97 |
| AHDB | Aug | -16 | 7.53 | 17.4 | 2.09 | 4.86 | 2.00 | 1.94 |
| AHDB | Aug | -20 | 7.5 | 14.9 | 1.98 | 2.05 | 1.73 | 1.70 |
| AHDB | Aug | -23 | 7.6 | 14 | 2.00 | | 2.20 | 0.65 |
| AHDB | Jan | 0 | 7.49 | 7.9 | 8.43 | 3.79 | 1.19 | 2.99 |
| AHDB | Jan | -5 | 7.49 | 7.4 | 7.70 | 2.97 | 1.31 | 2.60 |
| AHDB | Jan | -10 | 7.97 | 7.3 | 8.14 | 3.05 | 0.96 | 2.64 |
| AHDB | Jan | -15 | 7.95 | 7.1 | 8.76 | 1.46 | 0.80 | 2.66 |
| AHDB | Jan | -20 | 7.92 | 7.23 | 8.80 | 3.21 | 1.05 | 2.19 |
| AHDB | Jan | -23 | 7.9 | 7.3 | 8.33 | 2.56 | 0.82 | 2.67 |
| AHLJK | Aug | 0 | 8 | 25.1 | 7.80 | 6.08 | 3.00 | 1.65 |
| AHLJK | Aug | -3 | 7.8 | 22.1 | 6.51 | 5.82 | 3.20 | 1.78 |
| AHLJK | Aug | -6 | 7.6 | 19.2 | 2.33 | 5.75 | 2.40 | 1.29 |
| AHLJK | Aug | -9 | 7.5 | 18.6 | 1.65 | 6.11 | 2.50 | 1.20 |
| AHLJK | Aug | -13 | 7.6 | 14.2 | 1.60 | | 2.53 | 1.05 |
| AHLJK | Jan | 0 | 7.95 | 7.95 | 9.00 | 2.80 | 0.86 | 2.01 |
| AHLJK | Jan | -3 | 7.8 | 7.8 | 8.88 | 3.00 | 1.26 | 5.06 |
| AHLJK | Jan | -6 | 7.87 | 7.87 | 8.60 | 2.50 | 0.91 | 1.98 |
| AHLJK | Jan | -10 | 7.46 | 7.46 | 9.20 | 2.00 | 0.89 | 2.32 |
| HFHW | Aug | 0 | 9.37 | 28.1 | 8.10 | 42.10 | 3.73 | 1.48 |
| HFHW | Aug | -3 | 8.49 | 26.6 | 7.50 | 29.23 | 3.00 | 0.75 |
| HFHW | Aug | -6 | 8.42 | 26.3 | 5.20 | 21.06 | 3.00 | 1.55 |
| HFHW | Aug | -9 | 8.21 | 25.9 | 1.20 | 11.74 | 3.27 | 1.80 |
| HFHW | Aug | -12 | 7.66 | 24.1 | 1.10 | 7.50 | 2.60 | 1.67 |
| HFHW | Aug | -15 | 7.54 | 23.3 | 1.00 | 5.23 | 1.73 | 1.29 |
| HFHW | Aug | -19 | 7.44 | 22.6 | 1.20 | | 2.20 | 1.22 |
| HFHW | Jan | 0 | 8.31 | 8 | 15.00 | 9.91 | 2.59 | 2.13 |
| HFHW | Jan | -5 | 7.99 | 7.8 | 14.20 | 10.61 | 2.48 | 2.58 |
| HFHW | Jan | -10 | 8.13 | 8.1 | 14.00 | 10.52 | 1.40 | 2.15 |
| HFHW | Jan | -15 | 7.94 | 8 | 13.00 | 8.36 | 1.94 | 2.83 |
| HFHW | Jan | -20 | 8.18 | 7.8 | 12.00 | 8.34 | 1.87 | 5.69 |
| HFHW | Jan | -25 | 8.08 | 7.5 | 12.50 | 5.58 | 1.49 | 12.04 |
| HFDB | Jan | 0 | 7.75 | 8.1 | 12.10 | 7.30 | 1.09 | 2.44 |
| HFDB | Jan | -5 | 7.84 | 7.7 | 11.90 | 5.30 | 1.72 | 2.20 |
| HFDB | Jan | -10 | 7.81 | 7.8 | 11.80 | 6.50 | 1.27 | 3.94 |
| HFDB | Jan | -15 | 7.79 | 7.7 | 11.90 | 5.20 | 1.82 | 1.95 |
| HFDB | Jan | -20 | 7.51 | 7.7 | 12.10 | 4.90 | 1.54 | 3.21 |
| HFDB | Jan | -30 | 7.7 | 7.6 | 11.80 | 5.10 | 1.58 | 2.83 |

Table2: The Zn isotope composition, SPM Zn and $Al_2O_3$, and speciation Zn of SPM in summer and winter for Aha Lake and Hongfeng Lake.

| Sample site SPM | Date | Depth m | $Al_2O_3$(SPM) % | Zn(SPM) mg/g | AEC-Zn(SPM) % | organic-Zn(SPM) % | Residual-Zn(SPM) % | $\delta^{66}Zn_{IMC}$ (‰) | Zn/Al |
|---|---|---|---|---|---|---|---|---|---|
| AHDB | Aug | 0 | 4.44 | 0.26 | 70.23 | 16.05 | 13.72 | 0.10 | 0.0110 |
| AHDB | Aug | -4 | 0.37 | 0.30 | 74.26 | 19.04 | 6.69 | -0.05 | 0.1529 |
| AHDB | Aug | -8 | 3.11 | 0.32 | 68.00 | 23.90 | 8.10 | -0.03 | 0.0195 |
| AHDB | Aug | -12 | 1.57 | 0.40 | 86.87 | 9.04 | 4.09 | 0.02 | 0.0481 |
| AHDB | Aug | -16 | 0.80 | 0.48 | 78.59 | 18.49 | 2.92 | 0.01 | 0.1135 |
| AHDB | Aug | -20 | 1.57 | 0.70 | 66.67 | 23.25 | 10.08 | 0.02 | 0.0840 |
| AHDB | Aug | -23 | 1.23 | 0.32 | 86.80 | 9.73 | 3.47 | 0.19 | 0.0490 |
| AHDB | Jan | 0 | 5.14 | 0.36 | 86.42 | 4.04 | 9.55 | 0.16 | 0.0131 |
| AHDB | Jan | -5 | 5.24 | 0.57 | 79.07 | 15.46 | 5.47 | 0.23 | 0.0205 |
| AHDB | Jan | -10 | 6.45 | 0.27 | 83.66 | 8.42 | 7.92 | 0.27 | 0.0080 |
| AHDB | Jan | -15 | 1.28 | 0.25 | 87.69 | 5.43 | 6.89 | 0.21 | 0.0372 |
| AHDB | Jan | -20 | 4.01 | 0.40 | 94.72 | 3.86 | 1.42 | 0.55 | 0.0187 |
| AHDB | Jan | -23 | 3.05 | 0.27 | | | | 0.20 | 0.0167 |
| AHLJK | Aug | 0 | 0.62 | 0.38 | 59.37 | 18.38 | 22.25 | -0.18 | 0.1149 |
| AHLJK | Aug | -3 | 0.47 | 0.18 | 70.89 | 12.92 | 16.20 | 0.05 | 0.0738 |
| AHLJK | Aug | -6 | 1.46 | 0.24 | 86.92 | 12.24 | 0.83 | 0.12 | 0.0307 |
| AHLJK | Aug | -9 | 2.39 | 0.26 | 83.21 | 8.99 | 7.80 | 0.16 | 0.0203 |
| AHLJK | Aug | -13 | 1.17 | 0.32 | 57.36 | 19.50 | 23.14 | 0.09 | 0.0514 |
| AHLJK | Jan | 0 | 2.15 | 0.21 | 81.94 | 4.76 | 13.30 | 0.13 | 0.0187 |
| AHLJK | Jan | -3 | 2.65 | 0.69 | 76.91 | 8.83 | 14.26 | 0.03 | 0.0488 |
| AHLJK | Jan | -6 | 2.99 | 0.40 | 71.59 | 7.31 | 21.10 | 0.20 | 0.0254 |
| AHLJK | Jan | -10 | 2.85 | 0.32 | 75.64 | 5.56 | 18.80 | 0.14 | 0.0213 |
| HFHW | Aug | 0 | 2.15 | 0.39 | 54.69 | 9.10 | 36.21 | 0.20 | 0.0344 |
| HFHW | Aug | -3 | 6.44 | 0.48 | 52.01 | 11.26 | 36.73 | 0.01 | 0.0140 |
| HFHW | Aug | -6 | 3.28 | 0.34 | 29.13 | 53.14 | 17.73 | -0.11 | 0.0193 |
| HFHW | Aug | -9 | 5.13 | 0.60 | 75.72 | 7.59 | 16.69 | -0.19 | 0.0220 |
| HFHW | Aug | -12 | 6.58 | 0.35 | 80.71 | 5.82 | 13.47 | -0.29 | 0.0101 |
| HFHW | Aug | -15 | 5.17 | 0.29 | 84.00 | 5.65 | 10.35 | -0.20 | 0.0107 |
| HFHW | Aug | -19 | 5.89 | 0.52 | 81.80 | 7.69 | 10.50 | -0.11 | 0.0167 |
| HFHW | Jan | 0 | 4.75 | 0.40 | 83.39 | 6.12 | 10.48 | 0.15 | 0.0158 |
| HFHW | Jan | -5 | 4.29 | 0.24 | 78.95 | 10.84 | 10.21 | 0.10 | 0.0104 |
| HFHW | Jan | -10 | 5.22 | 0.31 | 86.33 | 5.26 | 8.40 | 0.12 | 0.0112 |
| HFHW | Jan | -15 | 8.77 | 0.30 | 81.88 | 4.74 | 13.38 | 0.22 | 0.0065 |
| HFHW | Jan | -20 | 10.41 | 0.75 | 84.66 | 5.97 | 9.38 | 0.26 | 0.0136 |
| HFHW | Jan | -25 | 12.02 | 0.48 | 75.27 | 12.77 | 11.95 | 0.13 | 0.0075 |
| HFDB | Jan | 0 | 4.76 | 0.30 | 89.07 | 6.01 | 4.92 | 0.11 | 0.0121 |
| HFDB | Jan | -5 | 4.56 | 0.34 | 86.79 | 5.40 | 7.80 | 0.20 | 0.0141 |
| HFDB | Jan | -10 | 4.30 | 0.38 | 89.36 | 4.64 | 6.00 | 0.07 | 0.0166 |
| HFDB | Jan | -15 | 5.37 | 0.40 | 90.08 | 4.63 | 5.29 | 0.17 | 0.0142 |
| HFDB | Jan | -20 | 5.02 | 0.35 | 82.15 | 12.06 | 5.79 | 0.12 | 0.0132 |
| HFDB | Jan | -30 | 4.70 | 0.34 | 88.66 | 5.08 | 6.26 | 0.22 | 0.0136 |
| | | | | | | | | | |
| Sampling | site station | | | | | | | | |
| Algae | MXR | | | | | | | 0.41 | |
| Aglea | MXR | | | | | | | 0.40 | |
| Plant | MXR | | | | | | | 0.21 | |

Table3. The pH, temperature, DO(dissolved oxygen), discharges, concentration of dissolved Zn, SPM and SPM Zn, and Zn isotope composition in tributaries of Aha Lake and Hongfeng Lake.

| Sampling site | Sampling | Average discharge $m^3/S$ | Draining In/Out | pH | T (℃) | Do mg/L | SPM mg/L | Zn-DIS μg/L | Zn-SPM mg/g | $AL_2O_3$ % | $\delta^{66}Zn_{JMC}$ ‰ | Zn/Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tributaries of | Aha Lake | | | | | | | | | | | |
| XCR | Aug | 0.65 | Out | 7.21 | 12 | 5.19 | 0.87 | 1.07 | 0.84 | 1.35 | 0.20 | 0.1166 |
| XCR | Jan | 0.65 | Out | 7.66 | 7.7 | 8.45 | 1.03 | 2.48 | 0.62 | 5.57 | 0.11 | 0.0212 |
| BYR | Aug | 0.90 | In | 8.14 | 21.8 | 7.47 | 4.53 | 1.53 | 0.26 | 5.64 | -0.17 | 0.0088 |
| BYR | Jan | 0.90 | In | 8.36 | 7.4 | 10.32 | 2.21 | 5.68 | 0.26 | 6.84 | 0.05 | 0.0073 |
| CCR | Aug | 0.21 | In | 7.66 | 21.6 | 5.19 | 6.27 | 1.42 | 0.93 | 4.99 | 0.34 | 0.0351 |
| CCR | Jan | 0.21 | In | 7.71 | 9.3 | 8.8 | 1.71 | 7.54 | 0.43 | 1.27 | 0.10 | 0.0635 |
| SR | Aug | 0.83 | In | 8.28 | 22.6 | 7.6 | 78.03 | 1.03 | 0.00 | | | |
| SR | Jan | 0.83 | In | 8.28 | 8.7 | 10.4 | 3.29 | 5.13 | 1.27 | 8.02 | 0.29 | 0.0299 |
| YYR | Aug | 1.18 | In | 8.18 | 21.6 | 8.17 | 65.93 | 18.07 | 0.49 | 1.24 | -0.09 | 0.0744 |
| YYR | Jan | 1.18 | In | 7.88 | 8.6 | 9.28 | 21.53 | 4.78 | 0.49 | 1.24 | 0.46 | 0.0744 |
| LNGR | Aug | 0.15 | In | 7.61 | 21 | 1.6 | 27.40 | 3.56 | 0.00 | 4.38 | | |
| LNGR | Jan | 0.15 | In | 7.14 | 8.7 | 5.11 | 14.00 | 11.30 | 0.51 | 3.17 | -0.04 | 0.0303 |
| Turbutaries of Hongfeng lake | | | | | | | | | | | | |
| MTR | Aug | 14.74 | Out | 7.49 | 20.7 | 5.98 | 0.93 | 1.48 | 0.19 | 1.21 | 0.22 | 0.0288 |
| MTR | Jan | 14.74 | Out | 7.42 | 6.9 | 6.91 | 1.48 | 2.95 | 0.48 | 5.38 | 0.10 | 0.0170 |
| THYR | Aug | 4.14 | In | 7.13 | 24.5 | 7.8 | 9.40 | 14.78 | 2.90 | 10.28 | 0.40 | 0.0533 |
| THYR | Jan | 4.14 | In | 7.29 | 5.6 | 9.23 | 4.91 | 5.31 | 1.83 | 7.49 | 0.25 | 0.0462 |
| YCR | Aug | 12.67 | In | 7.37 | 26.5 | 7.2 | 3.00 | 2.59 | 0.70 | 9.61 | 0.40 | 0.0137 |
| YCR | Jan | 12.67 | In | 7.08 | 3.4 | 10.2 | 3.42 | 12.42 | 0.43 | 5.79 | 0.04 | 0.0141 |
| MXR | Aug | 5.31 | In | 8.04 | 26.3 | 8.17 | 3.47 | 0.24 | 0.17 | 6.85 | 0.30 | 0.0048 |
| MXR | Jan | 5.31 | In | 7.67 | 4.2 | 10.38 | 0.91 | 2.46 | 0.25 | 6.06 | 0.48 | 0.0079 |
| HLR | Aug | 1.86 | In | 8.07 | 24.9 | 7.38 | 1.20 | 0.65 | 0.00 | | 0.03 | |
| HLR | Jan | 1.86 | In | 9.72 | 3.9 | 9.76 | 1.74 | 4.13 | 0.25 | 16.70 | 0.13 | 0.0028 |
| MBR | Jan | 0.32 | In | 7.44 | 9 | 8.32 | 1.93 | 3.94 | 0.46 | 12.44 | 0.14 | 0.0069 |